

2 Analysis of Variations in Ozone & Ozone Precursors

2.2 Ozone Precursor Trends in the South Coast Air Basin

2.2.1 Abstract

This chapter examines trends in ambient concentrations of ozone, carbon monoxide, and the various forms of oxides of nitrogen (NO_x) in the South Coast Air Basin (SoCAB) by day of the week from 1980 to 1997. Although volatile organic compounds (VOCs) are precursors to ozone, VOC trends are not presented here because long-term, good quality, continuous data are lacking.

Any hypothesis of a major factor contributing to the ozone weekend effect should be consistent with long-term trends as well as short-term (diurnal) variations. In this section, long-term trends are presented and examined for consistency with each hypothesis. Interpretation of the trends is hampered by the interference of year-to-year meteorological variations.

The trends tend to be similar for carbon monoxide and oxides of nitrogen on the same day-of-week at the same monitoring site. However, the trends are not the same at all monitoring sites. Concentrations at some sites exhibit flat precursor trends (primarily in the eastern portion of the SoCAB); other sites exhibit slow to moderate downward trends.

The trend in ozone concentrations was down at most sites but remained approximately flat at a few coastal sites (e.g., Hawthorne, Long Beach). The ozone trend was flat at several other coastal sites until the 1990s when the trend became downward. An interesting feature of the ozone trends in the eastern SoCAB was that the weekday concentrations have decreased faster than the weekend concentrations (e.g., San Bernardino, Upland).

Collectively, the trends are consistent with a faster rate of growth in the eastern basin than the western basin. Such growth would cause a slower rate by which emissions decrease in the eastern basin. The trends do not explicitly address the “carryover at the surface” hypothesis or the “carryover aloft” hypothesis. The results of this analysis do not support the “increased weekend emissions” hypothesis. However, the results are consistent with the “ NO_x -reduction” hypothesis and the “ NO_x -timing” hypothesis. The analysis does not directly address the “Soot and sunlight” hypothesis.

2.2.2 Introduction

A retrospective analysis of how ozone concentrations have changed over times with relatively different controls of ozone precursors provides an indication of how ozone concentrations may respond to future controls of ozone precursors. The South Coast Air Basin was chosen for this analysis because it experiences high ozone concentrations and has a large number of long-term monitoring sites in a

variety of settings. Evaluation of ozone trends in relation to ozone precursor trends can yield insights into the response of ozone concentrations to spatial and temporal changes in precursor emissions. By looking at trends by day-of-week and site, this analysis can help identify differences in emission patterns. Assuming emissions change equally for all periods of the day (i.e., scale factor change and not a spatial or temporal change), analysis of trending differences by period-of-day can yield insights into changes in chemistry.

2.2.3 Methodology

Hourly ozone (O_3), carbon monoxide (CO), oxides of nitrogen (NO_x), nitric oxide (NO), and nitrogen dioxide (NO_2) concentration data were retrieved from ARB's air quality database for the summers (May – October) of 1980 through 1997. These data were averaged by pollutant, monitoring site, year, day-of-week, and hour. Ideally, each mean represents 26 data values. For trending, values based on less than 20 observations were removed from the analysis and the data were further averaged into six 4-hour periods of the day (PODs), beginning at midnight. The midnight - 4 a.m. period provides information for assessing pollution carryover at ground level. The 4 a.m. - 8 a.m. period provides information for assessing emissions during the morning commute. The 8 a.m. - noon period provides information for assessing photochemistry and possibly carryover aloft. The noon - 4 p.m. period provides information on the conditions when the peak ozone concentrations occur. The 4 p.m. - 8 p.m. period provides information on the evening commute and the winding down of photochemical activity. The 8 p.m. - midnight period provides information on evening activity patterns and the potential for increased carryover of pollutants at ground level. For presentation purposes, the PODs for Tuesday, Wednesday, and Thursday were combined into a weekday mean; the Monday and Friday results were not plotted.

Measures of peak basin-wide ozone (e.g., annual maximum 1-hour concentration, mean of Top 30 daily maximum 1-hour concentrations, number of days with ozone concentrations exceeding various health levels) are also presented to identify the ozone response in the SoCAB to changes in emissions.

2.2.4 Results

Ozone concentrations are also presented to provide a context for interpretation of the precursor trends. As meteorology and emissions can vary spatially, the descriptions below are an attempt to characterize overall patterns common to multiple sites. A given site, in a given year, may lack some of the characteristics described.

2.2.4.1 Ozone (O_3)

2.2.4.1.1 Trend of SoCAB Peak Concentrations

The peak ozone concentrations in the SoCAB have declined over the years, irrespective of precursor control strategy (see Figures 2.2-1 and 2.2-2). VOC

emissions were controlled initially but NO_x emissions were also controlled beginning in the mid-1970s and have trended downward during the 1980s and 1990s.

2.2.4.1.2 Trends by Period-of-Day

O₃ concentrations are plotted for the mid-morning (4 a.m. – 8 a.m. PST), the late-morning period (8 a.m. – noon PST), and the early-afternoon period (noon – 4 p.m. PST) for the core set of monitoring sites. The mid-morning period provides an indication of the strength of ozone scavenging by fresh nitric oxide (NO) emissions; the late-morning period is representative of the O₃ build-up period; and the early-afternoon period represents the conditions when O₃ concentrations peak.

The O₃ trends are presented by monitoring site in the Figures section at the end of this chapter. Several features are apparent in many of the ozone trend plots. First, the day-of-week relationships are reversed from those of CO and NO_x; weekdays consistently have the lowest concentrations, Sundays have the highest concentrations, and Saturdays have intermediate concentrations. The differences between the days of the week become smaller from the late-morning period to the early-afternoon period.

Second, the year-to-year variations in O₃ concentrations are generally smaller for the robust weekday mean than the Saturday and Sunday means.

Third, although further smoothing and testing are warranted for trending, we make the following observations with the knowledge that 1996 and 1997 were El Niño years with better dispersion of pollutants. The overall late-morning trend of O₃ concentrations is downward at most sites; Hawthorne, Long Beach, and Lake Gregory are the exceptions with flat O₃ trends.

The average O₃ concentrations for the early-afternoon POD, are a few parts per hundred million higher than the concentrations for the late-morning POD. One difference between the late-morning and the early-afternoon PODs however is that sites in the eastern portion of the basin tend to have the highest ozone concentrations on Saturday in the early-afternoon but Sunday tended to have the highest concentrations in the late-morning POD. Thus, to some extent it appears that the O₃ concentrations at some sites continue to increase more from late morning into early afternoon on Saturdays than on Sundays in the eastern portion of the basin. It also appears that weekday concentrations have declined faster than weekend (especially Sunday) concentrations in the eastern portion of the air basin where the peak concentrations tend to occur. The relative difference between days of the week is smallest (weekday concentrations are often higher than the Sunday concentrations) at Lake Gregory, one of the high ozone sites in the basin. In essence, the weekend effect, which was noticeable primarily in the coastal region in the 1970s, has expanded eastward over the years and now encompasses most sites in the SoCAB.

Although ozone concentrations tend to be trending downward on all days of the week, the downward trend on Sundays, and to some extent on Saturdays, appears slower than on weekdays. Much of the decrease in the weekday concentration occurred between 1989 and 1990 at several sites and even seems like a stepwise change at some (e.g., Anaheim, Azusa). This large change from 1989 to 1990 is also apparent in the trends of other pollutants in some instances but the 1991 levels tend to rebound close to the 1989 levels. Further investigation is warranted into the meteorological, chemical, and other factors that may be contributing to this large year-to-year change.

Except for Lake Gregory, early-morning O₃ concentrations are low (presumably due to scavenging by NO and deposition), the concentrations are very similar by day-of-week, and the trends are flat. Mid-morning O₃ concentrations on the other hand begin to separate by day-of-week. At many locations, the separation appears due to greater NO titration on weekdays than on Saturdays than on Sundays as concentrations decrease from early-morning to mid-morning. At locations with relatively low NO_x emissions, the mid-morning O₃ concentrations on Sunday have already begun increasing. This early increase in ozone concentrations on Sundays is consistent with the diurnal profiles in the previous chapter and indicates that ozone formation is exceeding scavenging by NO. This pattern is consistent with the NO_x-reduction hypothesis, the NO_x-timing hypothesis, and the carryover aloft hypothesis.

Some of the ozone data were further summarized to describe the spatial and temporal changes in the weekend effect. Figures showing the percent difference in Sunday and Saturday concentrations compared to mid-week concentrations are presented for the late-morning and early-PM periods of the day in Figures 2.2-87 and 2.2-88 for the Azusa, Los Angeles, and Riverside monitoring sites for 1982, 1988, and 1995. The results show that the weekend effect is much stronger in 1995 and that Sunday is the peak ozone day during the late-morning period but that Saturday is slightly higher than Sunday as the peak day in the afternoon period. The greater differentiation between Saturday and Sunday during the late-morning period compared to the afternoon period may support the NO_x-timing hypothesis. The greater emissions during late-morning on Saturday compared to Sunday may initially slow down the ozone formation (e.g., NO_x-scavenging, radical termination) but injects more NO such that when the new equilibrium is established, more ozone is produced throughout Saturday afternoon than throughout Sunday afternoon.

2.2.4.2 Carbon Monoxide (CO)

CO concentrations are quite low during the summer and the POD results are plotted only for the mid-morning period (4 a.m. – 8 a.m. PST) for the core set of monitoring sites. The CO trends are incomplete at some monitoring sites because of site relocations or discontinued CO monitoring at sites with low concentrations in an attempt to cut costs. The mid-morning period is representative of the morning commute period and represents the initial conditions when photochemical reactions begin.

The CO trends are presented by monitoring site in the Figures section at the end of this chapter. Several features are apparent in many of the trend plots. First, the day-of-week relationships are very consistent with weekdays having the highest concentrations, Sundays having the lowest concentrations, and Saturdays having intermediate concentrations levels. The Saturday values appear to be closer to the Sunday values in central Los Angeles County and to be closer to the weekday values in the outlying areas.

Second, the year-to-year variations generally apply to all three days of the week and likely reflect local seasonal weather differences (e.g., higher frequency of fog or warm temperatures than normal). As one might expect based on the smaller sample size, the seasonal CO concentration values for Saturday and Sunday exhibit more variability than the weekday mean. Any consistent shift in the relationship between the days may reflect a change in day-of-week activity patterns.

Third, although further smoothing and testing are warranted for trending, we make the following observations with the knowledge that 1996 and 1997 were El Niño years with better dispersion of pollutants but also include an approximate 15 percent decrease in response to changes in gasoline composition. The overall pattern of CO concentrations appears to be flat since 1981 at Anaheim, Azusa, Los Angeles, Lynwood, and Riverside; and down in the 1980s but flat in the 1990s at Burbank, Hawthorne, Long Beach, and possibly San Bernardino and Upland;

Lastly, about half of the monitoring sites had concentrations 2-3 times higher in 1980 than in subsequent years. This difference is much larger than the typical year-to-year variation and needs to be investigated further to determine the cause (e.g., erroneous data, calibration shift, meteorology, emission controls). A likely cause is one or two months of data having an incorrect code for the measurement unit (e.g., ppm instead of pptm).

The CO trends do not specifically address the weekend effect hypotheses. As a relatively long-lived, primary pollutant, the CO concentrations provide an indication of the overall seasonal influence of variable meteorological conditions. The trend plots do not provide supporting evidence for the increased weekend emissions hypothesis as weekend CO concentrations were lower throughout the day than weekday concentrations. The temporal resolution of the POD analysis may be too crude to address the carryover hypotheses. The CO trends do not shed additional light on the NO_x-reduction and NO_x-timing hypotheses.

2.2.4.3 Oxides of Nitrogen (NO_x)

NO_x concentrations are quite low during the summer and the POD results are plotted for the mid-morning period (4 a.m. – 8 a.m. PST), the late-morning period (8 a.m. - noon PST), and the mid-day (afternoon or early PM; noon - 4 p.m. PST) period for the core set of monitoring sites. The mid-morning period is representative of the morning commute period and represents the initial conditions when photochemical reactions begin; the late-morning period represents conditions during active

photochemistry: and the mid-day period represents conditions during the period of peak ozone concentrations.

The NO_x trends are presented by monitoring site in the Figures section at the end of this chapter. Several features are apparent in many of the trend plots. First, the day-of-week relationships are very consistent with weekdays having the highest concentrations, Sundays having the lowest concentrations, and Saturdays having intermediate concentrations.

Second, unlike the CO values, the year-to-year variations do not generally apply to all three days of the week; apparently, the NO_x values do not solely reflect the changes in dispersion associated with local seasonal weather differences but also any variations in photochemistry paths and rates. Unlike the CO situation, the seasonal NO_x concentration values for the robust weekday mean exhibited almost as much variability as the Saturday mean and more variability than the Sunday mean.

Third, although further smoothing and testing are warranted for trending, we make the following observations with the knowledge that 1996 and 1997 were El Niño years with better dispersion of pollutants. The overall trend of NO_x concentrations on weekdays appears to be flat or slowly decreasing (however, Upland appears to have had a step increase in 1987). The overall trend of NO_x concentrations on weekends appears to be decreasing at a slightly faster rate than on weekdays.

The trend of mid-morning NO_x concentrations is often flat in the 1990s but NO_x concentrations for the late-morning POD are slightly lower and less variable than those for the mid-morning POD. Slight downward trends are generally evident (Long Beach and Los Angeles trends are obvious) except in at sites in the eastern basin where the trends appear to be flat. However, the afternoon (early-PM) NO_x concentrations trend downward at several sites.

As a primary precursor of ozone, the NO_x trends can address the weekend effect hypotheses. The trend plots do not provide supporting evidence for the increased weekend emissions hypothesis as weekend NO_x concentrations were lower throughout the day than weekday concentrations. The temporal resolution of the POD analysis may be too crude to address the carryover aloft hypothesis; carryover of NO_x is not anticipated to be significant compared to carryover of ozone and volatile organic compounds (VOCs).

By themselves, the NO_x trends shed little light on the NO_x-reduction and NO_x-timing hypotheses. The NO_x-reduction hypothesis focuses on changes in the VOC/NO_x ratio rather than the change in NO_x alone. The NO_x-timing hypothesis focuses on differences in the pattern of emissions within the day. The differences may remain unchanged while trends increase or decrease.

2.2.4.4 Nitrogen Dioxide (NO₂)

NO₂ concentrations are lower during the summer than during the fall because the photolysis limits the accumulation of NO₂. POD results are plotted for the late-morning period (8 a.m. – noon PST) and the early-afternoon period (noon – 4 p.m. PST) for the core set of monitoring sites. The late-morning period is representative of the NO₂ build-up period and the “fuel” available for ozone generation. The early-afternoon period represents the conditions when ozone production is greatest.

The NO₂ trends are presented by monitoring site in the Figures section at the end of this chapter. Several features are apparent in many of the trend plots. First, the day-of-week relationships are very consistent with weekdays having the highest concentrations, Sundays having the lowest concentrations, and Saturdays having intermediate concentrations.

Second, the year-to-year variations are generally smaller than observed for the NO_x values, as might be expected. The seasonal NO₂ concentration values for the robust weekday mean exhibited almost as much variability as the Saturday mean and more variability than the Sunday mean.

Third, although further smoothing and testing are warranted for trending, we make the following observations with the knowledge that 1996 and 1997 were El Niño years with better dispersion of pollutants. The overall trends of NO₂ concentrations are downward at most sites in the western and central SoCAB and flat in the eastern portion of the basin. The decline is fastest at the Long Beach site. At a few sites (e.g., Azusa) the weekday and Saturday trends appear flat in the 1990s.

NO₂ concentrations for the early-afternoon POD, although slightly lower than concentrations for the late-morning POD, exhibit a similar pattern with varying degrees of downward trends in the western SoCAB and somewhat flat trends in the eastern basin. The NO₂ trends generally follow the NO_x trends closely by day-of-week. Thus, there is little evidence for a change in the chemistry of NO₂ formation.

As the source of oxygen atoms for ozone formation, the NO₂ trends can address the weekend effect hypotheses. The trend plots do not provide supporting evidence for the increased weekend emissions hypothesis as weekend NO₂ concentrations were lower throughout the day than weekday concentrations. The temporal resolution of the POD analysis may be too crude to address the carryover aloft hypothesis; carryover of NO₂ is not anticipated to be significant compared to carryover of ozone and volatile organic compounds (VOCs). Although year-to-year variability is still significant for NO₂, the trends appear similar by day-of-week and period-of-day. Thus, the NO₂ trends do not shed additional light on the NO_x-reduction and NO_x-timing hypotheses.

2.2.5 Conclusions

Although simple and qualitative, this initial characterization of ozone and ozone precursor trends by period of the day yielded fairly consistent results despite the

year-to-year “noise” caused by meteorological variations. The trend of peak ozone concentrations in the SoCAB has been downward irrespective of the focus of the precursor control program. It is also interesting to note that the day of the week with the peak ozone concentration has apparently “crossed over” from Thursday and Friday in the 1960s and 1970s at all but coastal sites to Weekends (first Saturday and more recently Sunday) at almost all sites in the SoCAB by the end of the 1990s. The ozone weekend effect has been particularly large in the 1990s. The weekend effect appears to be growing larger and more widespread over time in the SoCAB.

The trends by day-of-week and period-of-day do not support the increased emissions hypothesis. Although there is some evidence of boundary-layer carryover of NO_x on Saturday mornings in the early years, the day-of-week differences became small in the 1990s. The trend analyses are too crude to assess the presence and significance of carryover aloft.

2.2.6 Recommendations

The analysis identified some large, stepwise changes which warrant further investigation and illustrate the importance of a good quality assurance program and high precision instruments as ambient concentrations approach detection limits. Our recommendations are as follows:

- 1) Use techniques to smooth or to minimize some of the year-to-year variations in meteorology and its influence on ambient concentrations.
- 2) High quality data for VOCs should be collected routinely at several locations. Although trends from such measurements would not be meaningful for several years, the VOC data should be analyzed in other respects when available.